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Oxidation of α-Haloketones: Part I—V(V) Oxidation of Phenacyl Bromide & *p*-Nitrophenacyl Bromide

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The oxidation of phenacyl bromide and *p*-nitrophenacyl bromide by V(V) has been found to be of first order both in [oxidant] and [substrate]. The acid dependence of oxidation can be expressed by the equations: log $k = 0{\cdot}17 \times 10^{-4} - 3$ log $[HClO_4]$ and log $k = 0{\cdot}66 \times 10^{-4} - 2$ log $[H_2SO_4]$, in $HClO_4$ and H_2SO_4 respectively for phenacyl bromide. The inverse plot of rate constant (k) versus [phenacyl bromide] indicates a complex formation between substrate and the oxidant. The decomposition rate (k_3) of the complex is faster in the case of phenacyl bromide than in the case of *p*-nitrophenacyl bromide. However, the rate of oxidation (k) of *p*-nitrophenacyl bromide is found to be 2·5-3·0 times higher than that of phenacyl bromide. In the absence of any evidence for the formation of free radicals, a mechanism involving a concerted two equivalent process has been proposed.

OXIDANTS such as Ce(IV), permanganate, Cr(VI) in the presence of acid, and alkaline ferricyanide have been used for the oxidation of ketones[1]. All these studies have concluded that one-electron oxidants attack the enol tautomer and not the ketone directly[2]. However, subsequent work on the Co(III) and V(V) oxidations of cyclohexanone suggested a direct attack of oxidant on the ketone rather than on the enol[3]. Isotopic studies have also provided evidence in favour of this mechanism. Since aromatic ketones have not been subjected to oxidation studies to a large extent, the present work has been undertaken to study the nature of oxidation in aromatic ketones. The results are reported in this paper.

Materials and Methods

Acetic and sulphuric acids used were of Analar grade. Phenacyl bromide, m.p. 51°, prepared by the bromination of acetophenone and *p*-nitrophenacyl bromide (m.p. 91°), also prepared similarly, recrystallized from pet. ether and benzene before use. Their solutions were prepared in gl. acetic acid.

Sodium vanadate (BDH, Analar) solution was prepared in analar H_2SO_4 or $HClO_4$ of appropriate strength.

Kinetic measurements — The solutions of V(V) and the substrate were thermostated at appropriate temperature (±0·1°C) for 30 min and the reaction was initiated by mixing in a brown-coloured bottle. Aliquots (5 ml) of the reaction mixture were withdrawn into chilled H_2SO_4 solution, and titrated immediately against ferrous ammonium sulphate solution using N-phenylanthranilic acid as indicator. The rate constants were calculated using the second order rate expression.

Analysis of oxidation products — (V)V and the excess of phenacyl bromide were mixed and kept for several days till the solution completely changed to green colour. Thereafter, the solution was diluted with water and extracted several times with benzene. The benzene extract was neutralized with aq. $NaHCO_3$ solution, and the bicarbonate layer on acidification and cooling deposited white crystals of benzoic acid. The neutral benzene layer on TLC (silica gel) in benzene gave two spots (R_f 0 and 0·75). The compound having R_f 0 could not be identified and was believed to be polymeric. The compound with R_f 0·75 was identified (Co-TLC) as phenacyl bromide. In the same way *p*-nitrobenzoic acid was isolated from the oxidation of *p*-nitrophenacyl bromide. In this case the aq. layer (after extraction with benzene) was found to contain formaldehyde, which was identified as its 2,4-DNP derivative (m.p. 164°; lit. m.p. 167°).

Results and Discussion

Phenacyl bromide was found to consume two equivalents of V(V) in 3·0*M* $HClO_4$ at 35°. The second order rate expression (1) was used to evaluate the bimolecular rate constants (k_2).

$$t = \frac{2{\cdot}303}{k_2(a-b)} \log \frac{b(a-x)}{a(b-x)} \qquad \ldots(1)$$

Duplicate experiments were reproducible within ±3%. The rates (k_2) were evaluated at constant [substrate] and varying [V(V)] and the vice versa. In each case the values of k_2 were found to be constant. The first order rate constants (k_1) were also evaluated in those cases where [substrate] $\gg$[V(V)] and then converted into k_2. A plot of $1/k_1$ versus 1/[substrate] was not found to pass through the origin (Fig. 1). The energy of activation was calculated from the slope of the plot of log k_2 versus $1/T$.

The effect of varying [acid] on the reaction rate of phenacyl bromide was studied. The values of k were found to increase with increasing $[H_2SO_4]$

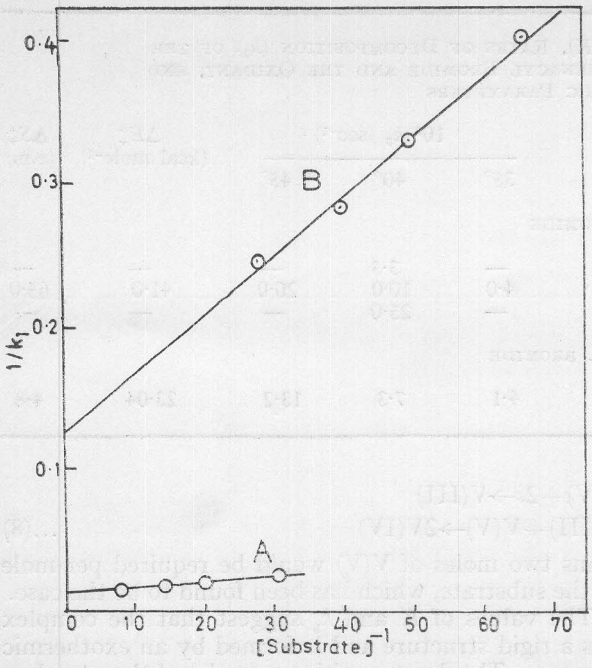


Fig. 1 — Plots of $1/k$ versus [substrate] for the oxidation of phenacyl bromide (curve A), and *p*-nitrophenacyl bromide (curve B) {[V(V)]=$31{\cdot}75\times10^{-3}M$ for phenacyl bromide and $6{\cdot}0\times10^{-3}M$ for *p*-nitrophenacyl bromide; [$HClO_4$]=$3{\cdot}0M$, AcOH=50% (v/v ; temp.=40°C}

(Table 1) and [$HClO_4$] (Table 2). The plots of log$k$ versus log [acid] were linear both in $HClO_4$ and H_2SO_4 obeying the Eqs. (2) and (3).

$$\log k = 0{\cdot}17\times10^{-4}-3\ \log\ [HClO_4] \qquad ...(2)$$

$$\log k = 0{\cdot}66\times10^{-4}-2\ \log\ [H_2SO_4] \qquad ...(3)$$

The plots of k versus $[HClO_4]^2$ and $[H_2SO_4]^3$ were linear but did not pass through the origing, indicating complexation of the oxidant with acid. A linear log-log plot, however, suggested the participation of a molecule of water.

The values of k and $1/D$ (ref. 4) are recorded in Table 3. The plot of log k_2 verrus $1/D$ was linear with a slope of +45·0, indicating that the oxidation takes place between an ion and a diplole. The positive ions may be designated as $[V(OSO_3H)]^+$, $[V(OH)HSO_4]^+$, and $[VO(OSO_3H)]^+$ as suggested by Littler and Waters[5]. Vanadium(V) in aq. AcOH has been described to exist as VO^+ (aq.) (ref. 6) and $V(OH)_4^+$ (ref. 7). The equilibria (4-7) have been suggested in $HClO_4$ and H_2SO_4 media.

$$VO_2^+ + 2H^+ \overset{K_1}{\rightleftharpoons} [V(OH)_2]^{3+} \qquad ...(4)$$

$$VO_2^+ + H_3O^+ \overset{K_2}{\rightleftharpoons} [V(OH)_3]^{2+} \qquad ...(5)$$

$$[V(OH)_2]^{+3} + HSO_4^- \overset{K_3}{\rightleftharpoons} [V(OH)_2HSO_4]^{2+} \qquad ...(6)$$

$$[V(OH)_3]^{++} + HSO_4^- \overset{K_4}{\rightleftharpoons} [V(OH)_3HSO_4]^{+} \qquad ...(7)$$

The equilibria (4) and (5) occur in $HClO_4$ and (6) and (7) in H_2SO_4. At lower [acid], the values of k in $HClO_4$ and H_2SO_4 are almost the same but at higher [acid] the rate constants (k) in $HClO_4$ are higher than in H_2SO_4 of comparable concentration.

TABLE 1 — EFFECT OF VARYING [H_2SO_4] ON V(V) OXIDATION OF PEHNACYL BROMIDE

{[V(V)]=$18{\cdot}88\times10^{-3}M$; [phenacyl bromide]=$125{\cdot}0\times10^{-3}M$; AcOH=50% (v/v); temp.=40°}

[H_2SO_4] M	$k\times10^4$ (litre mole^{-1} sec^{-1})
4·5	13·90
4·0	9·62
3·5	7·52
2·5	3·36
2·0	2·25

TABLE 2 — EFFECT OF VARYING [$HClO_4$], [PHENACYL BROMIDE] AND TEMPERATURE ON THE OXIDATION RATE OF PHENACYL BROMIDE

{[V(V)]=$31{\cdot}75\times10^{-3}M$; AcOH=50% (v/v)}

Temp. °C	[$HClO_4$] M	$k\times10^4$ (litre mole^{-1} sec^{-1}) at A	B	C	D
40	2·2	19·85	20·79	21·56	20·86
40	3·4	76·95	77·0	76·8	74·92
40	3·0	52·65	52·82	53·5	52·90
45	3·0	83·07	85·02	88·8	85·67
35	3·0	35·75	35·0	36·22	—

A, [Phenacyl bromide]=$125\times10^{-3}M$.
B, [Phenacyl bromide]=$93{\cdot}7\times10^{-3}M$.
C, [Phenacyl bromide]=$62{\cdot}5\times10^{-3}M$.
D, [Phenacyl bromide]=$106{\cdot}25\times10^{-3}M$.

TABLE 3 — EFFECT OF VARYING DIELECTRIC CONSTANT

{[V(V)]=$32{\cdot}25\times10^{-3}M$; [phenacyl bromide]=$62{\cdot}5\times10^{-3}M$; [$H_2SO_4$]=$2{\cdot}0M$}

%AcOH (v/v)	$1/D\times10^3$	$k\times10^4$ (litre mole^{-1} sec^{-1})
70	37·5	52·85
65	33·5	41·18
60	31·7	32·98
50	26·04	32·14
45	24·10	14·52
40	22·38	10·82

Since the plot of k_{obs}^{-1} versus [phenacyl bromide]$^{-1}$ did not pass through the origin, the values of equilibrium constants (K), the rates (k_3) of decomposition of the complex were determined at various temperatures and [acid]. The values are given in Table 4.

The decrease in free energy of formation of the complex was calculated from the relation: $+\Delta G = -RT\ \ln K$. The enthalpy change (ΔH) associated with K was calculated from the slope of the plot of log K verus $1/T$. It was used in the evaluation of ΔG from the relation: $\Delta G=\Delta H-T\Delta S$. The values of ΔH are given in Table 4.

Similarly from the values of k_3 at various temperatures, the energy ($\Delta E^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation (Table 4) for the decomposition process of the complex were determined.

The rate constants at different [substrate] have also been determined for *p*-nitrophenacyl bromide (Table 5). In this case also there is a kinetic evidence of complexation. Various thermodynamic

TABLE 4 — VALUES OF EQUILIBRIUM CONSTANTS (K), RATES OF DECOMPOSITION (k_3) OF THE COMPLEX BETWEEN PHENACYLBROMIDE, p-NITROPHENACYL BROMIDE AND THE OXIDANT, AND VARIOUS THERMODYNAMIC PARAMETERS

$[HClO_4]$	K (litre mole^{-1})			ΔH (kcal mole^{-1})	$-\Delta S$ (e.u.)	$10^3\ k_3$ (sec^{-1})			$\Delta E^{\ddagger}$ (kcal mole^{-1})	$\Delta S^{\ddagger}$ (e.u.)
	35°	40°	45°			35°	40°	45°		
					PHENACYL BROMIDE					
2·2	—	5·6	—	—	—	—	3·3	—	—	—
3·0	9·2	4·5	3·7	−18·4	55·4	4·0	10·0	20·0	41·0	65·0
3·4	—	2·3	—	—	—	—	25·0	—	—	—
					p-NITROPHENACYL BROMIDE					
3·0	25·4	16·6	11·5	−14·7	23·6	4·1	7·3	13·2	23·04	4·8

TABLE 5 — EFFECT OF VARYING TEMPERATURE, AND [p-NITROPHENACYL BROMIDE] ON THE OXIDATION RATE (k) OF THE HALOKETONE

{$[V(V)]=6·0\times10^{-3}M$; $[HClO_4]=3·0M$; AcOH=50% (v/v)}

[p-Nitrophenacyl bromide] $\times10^2$ (M)	$k\times10^4$ (litre mole^{-1} sec^{-1}) at 35°	40°	45°
3·0	11·17	14·68	20·00
2·5	10·96	14·68	21·54
2·0	11·45	15·03	20·84
1·5	11·60	15·66	21·32

parameters determined for the oxidation of p-nitrophenacyl bromide are given in Table 4. The rate of the reaction was found to be almost 2·5-3·0 times faster than that of phenacyl bromide. The values of ΔE are also in accordance with the reactivity of p-nitrophenacyl bromide. The values of $\Delta S^{\ddagger}$ are negative indicating a rigid transition state.

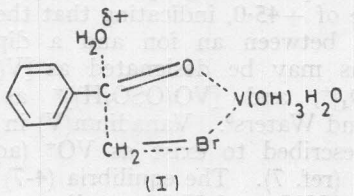
Vanadium(V) is a one-electron oxidant and also produces free radicals of the substrate. The formation of free radical was not indicated in the present study since polymerization with acrylonitrile or reduction of mercuric chloride could not be observed. Therefore, the present reaction is believed to proceed through an ionic intermediate, and V(V) probably acts as a two-electron oxidant according to Eq. (8) in $HClO_4$. The same observation was also recorded by Sengupta and coworkers[8].

$$V(V)+2e\rightarrow V(III)$$
$$V(III)+V(V)\rightarrow 2V(IV) \qquad \ldots(8)$$

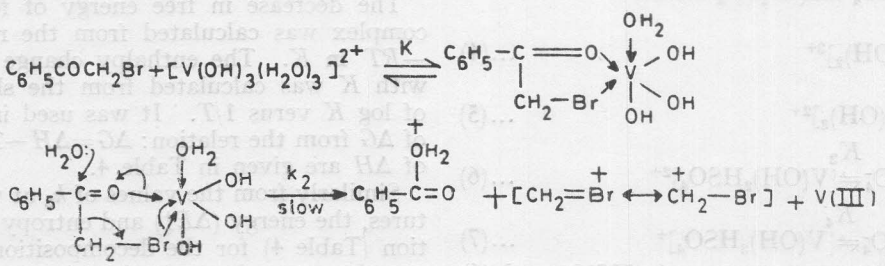
Thus two moles of V(V) would be required per mole of the substrate, which has been found to be the case.

The values of K and k_3 suggest that the complex has a rigid structure and is formed by an exothermic process. The decomposition rate (k_3) of the complex, however, was found to be faster in the case of phenacyl bromide than in the case of p-nitrophenacyl bromide, although the reverse was the case for the composite rate constant (k). The complex formation, however, was facilitated by the nitro substituent. From these considerations and from the fact that a molecule of water participates in the transition state, Scheme 1 can be suggested for the oxidation. Vanadium(V) forms octahedral complexes and there is a weak dipole-dipole type of interaction between the metal ion and water molecules. Therefore the complex formation will occur by replacement of water molecules.

The above mechanism (Scheme 1) involves the transition state (I), and appears to be similar to that proposed for V(V) oxidation of pinacols. The oxidation of pinacols also proceeds through C-C bond cleavage, but by a free radical pathway[1].



(I)



Scheme 1

The present oxidation does not appear to proceed through an enol intermediate because (i) the substituent effect is opposite to the acid-catalysed enolization (halogenation), and (ii) the value of equilibrium constant (K) for the formation of complex is higher for *p*-nitrophenacyl bromide than for phenacyl bromide.

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